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(54) SEPARATOR FOR SEALED LEAD STORAGE BATTERY

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a separator for sealed lead storage battery which can be made thinner, and a result, can improve high-rate discharge characteristics without hike in material cost or increase of electric resistance, making hole structure complex and like a maze, by intervention of dendrite-short-prevention agent in the gap of glass mat constituting a separator.

SOLUTION: This sealed lead storage battery has an inorganic powder substance interposed in a dispersed state in a sheet made mainly of fine glass fiber made through a simple wet-type process. The inorganic powder substance is fixed in gaps of the sheet by a water soluble inorganic salt.

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DETAILED DESCRIPTION

[Detailed description]

[0001]

[The technical field to which invention belongs] this invention relates to the separator for sealed type lead accumulators.

[0002]

[Prior art] Conventionally, there is a fiberglass-mat separator which made the subject the detailed glass fiber which serves as the duty as a retainer of the sulfuric-acid electrolytic solution, and ****ed it as a separator used for a sealed type lead accumulator. On the other hand, a sealed type lead accumulator begins the backup power supply of a portable device, a cordless device, and a computer in recent years, an electric vehicle and its intended use are greatly expanded to the large-sized cell for deferment, and the pan, and the sealed type lead accumulator is asked for much more enhancement in a high-rate-discharge property with high capacity-ization in connection with this. for this reason -- being alike -- it is necessary for a sealed type lead accumulator to make a plate thin, and to increase the plate number of sheets per cell cell, and to narrow a plate spacing, and the separator used there is also asked for thin shape-ization However, when a plate spacing is narrowed and a separator is thin-shape-ized, it becomes easy to generate the shunt (dendrite short-circuit) by the arborescence lead at the time of the low specific gravity of the electrolytic solution. For this reason, in order to high-capacity-ize a sealed type lead accumulator and to raise a high-rate-discharge property, it is required to equip the thin-shape-ized retainer separator with short-proof nature. There is the following technique as the technique of suppressing occurrence of dendrite short-circuit such inside a separator conventionally.

(1) There is the technique (Provisional Publication No. 54-22530 etc.) of making small the diameter of fiber of the glass fiber used for ****. By this technique, it can prevent that the dendrite which grows by making the aperture of a fiberglass-mat separator small penetrates a separator.

(2) Moreover, there is the technique (Provisional Publication No. 54-22530) of making it into the thickness more than fixed to the positive-electrode plate thickness which uses the thickness of a fiberglass-mat separator. By this technique, time until the dendrite which grows penetrates a separator by enlarging thickness of a fiberglass-mat separator can be earned.

(3) Moreover, there is the technique (Provisional Publication No. 54-50840 etc.) of making two-layer the fiberglass mat used for a separator, and putting the microporosity film which becomes the interlayer from synthetic resin etc., and making it into a sandwich structure. By this technique, since the film of microporosity is prepared for the interlayer and the dendrite which grows is intercepted in the parvus film layer of an aperture, it can prevent penetrating a separator.

(4) Moreover, the fiberglass mat used for a separator is made to carry out impregnation adhesion of the inorganic fine particles, the growth path of a dendrite is extension-ized by making inorganic fine particles intervene in the void of a fiberglass mat, and there are some which raised penetration shunt nature (publication number 260335 [11 to]).

[0003]

[Object of the Invention] However, there are the following troubles by the technique of preventing dendrite short-circuit of these former.

(1) It becomes a rise of a material cost to use the glass fiber of the thin diameter of fiber. Moreover, by this technique, the prevention effect of dendrite short-circuit is low, and a remarkable effect

cannot be desired.

(2) Thickening thickness of a fiberglass-mat separator moves against the purpose (thin-shape-izing) of invention.

(3) By the technique of making it into the three-tiered structure which arranged the microporosity film on the interlayer, a limitation will arise from being forced very cruel conditions in the present industrial technical level which the fiberglass-mat sheet of a simple substance needs to **** the thing of 1/2 more or less thickness, and ****s the fiberglass-mat sheet of the thin thickness corresponding to this in this invention aiming at thin-shape-izing in pursuit of thin-shape-izing naturally. Moreover, since the diffusibility of the electrolytic solution gets worse the electric resistance of a separator with slight height, arranging a microporosity film is connected with reducing a high-rate-discharge performance.

(4) By the technique of making inorganic fine particles adhering into a fiberglass mat, although the depressor effect of dendrite short-circuit is large, since it is making inorganic fine particles adhere independently, its powder omission is large in the time of a width-of-face decision manipulation of a separator, and the case of roll product rewinding, and a difficulty is in the workability at the time of cell assembly at them.

[0004] It is made in order that this invention may solve the trouble of such conventional technique. Thickness can be thin-shape-ized, without making a material cost raise or raising electric resistance. It is the separator for sealed type lead accumulators which can raise the high-rate-discharge property of a cell as a result. It is a thing aiming at forming structure into a complicated maze. making a dendrite-proof short inhibitor intervene in the void of the fiberglass mat which constitutes a separator -- a hole -- And it aims at offering the separator for sealed type lead accumulators which does not produce powder omission at the time of the handling of a separator.

[0005]

[The means for solving a technical problem] That the separator for sealed type lead accumulators of this invention should attain the aforementioned purpose, as claim 1 publication, it is the separator for sealed type lead accumulators which made inorganic fine particles placed between the sheets of the detailed glass fiber subject which carried out wet **** and was obtained in the state of variance, and is characterized by these inorganic fine particles being fixed by water-soluble mineral in the void of this sheet. Moreover, it is characterized by the separator for sealed type lead accumulators of claim 2 publication existing in the separator for sealed type lead accumulators of claim 1 publication, after the aforementioned water-soluble mineral has mainly been ****ed by the aforementioned inorganic fine-particles front face. Moreover, the separator for sealed type lead accumulators of claim 3 publication is characterized by the amount of the aforementioned inorganic fine particles being five to 50 capacity [of the pure volume of a separator] % in the claim 1 or the separator for sealed type lead accumulators given in two. Moreover, in the claim 1 or the separator for sealed type lead accumulators given in either of 3, the aforementioned inorganic fine particles are electric insulations, and the separator for sealed type lead accumulators of claim 4 publication is characterized by being the inorganic fine particles of sulfuric-acid-proof solubility. Moreover, the separator for sealed type lead accumulators of claim 5 publication is characterized by the aforementioned inorganic fine particles being a silica, an alumina, or a titania in the separator for sealed type lead accumulators of claim 4 publication. Moreover, the separator for sealed type lead accumulators of claim 6 publication is characterized by the particle diameter of the aforementioned inorganic fine particles being 5 micrometers or less in the claim 1 or the separator for sealed type lead accumulators given in either of 5. Moreover, the separator for sealed type lead accumulators of claim 7 publication is characterized by the aforementioned water-soluble mineral being the sulfate which acts as a short inhibitor in the claim 1 or the separator for sealed type lead accumulators given in either of 6. Moreover, it is characterized by the aforementioned water-soluble mineral containing the separator for sealed type lead accumulators of claim 8 publication 0.5 to 10% of the weight to the separator weight in an inorganic fine-particles lump in the claim 1 or the separator for sealed type lead accumulators given in either of 7. Moreover, it is characterized by the separator for sealed type lead accumulators of claim 9 publication being what is obtained by carrying out impregnation processing of the fiberglass-mat sheet which considered as the main material, carried out wet **** of the detailed glass fiber, and obtained it in the claim 1 or the separator for sealed type lead accumulators

given in either of 8; and drying it in the liquid which distributed and prepared inorganic fine particles and water-soluble mineral. Moreover, in the separator for sealed type lead accumulators of claim 9 publication, the separator for sealed type lead accumulators of claim 10 publication is characterized by carrying out impregnation processing at the liquid which distributed inorganic fine particles and water-soluble mineral, and was prepared so that it may become [sheet / fiberglass-mat / aforementioned] 1 - 9 % of the weight in the concentration of inorganic fine particles about the concentration of 1 - 15 % of the weight, and water-soluble mineral.

[0006]

[Gestalt of implementation of invention] the glass fiber used for the separator for sealed type lead accumulators of this invention has an independent diameter of mean fiber in the ** alkali detailed glass fiber which is 0.5-4 micrometers -- or two or more kinds can be mixed and it can use Moreover, although you may constitute only from a glass fiber when carrying out wet **** of the sheet of a glass fiber subject from the glass fiber of the above-mentioned diameter of mean fiber, the piece resistance by the grid edge which constitutes the plate at the time of high pressurization assembly may be raised, or organic fiber may be made to contain to 20 % of the weight for the purpose of improving the intensity of the U character bending section. The polyolefine which has acid resistance, polyester, or an acrylic fiber can be used for the organic fiber used here. If heat weld type fiber is used, it is more suitable from the ability to improve a strength property more.

[0007] moreover, the whole for the pore by which the inorganic fine particles used for the separator for sealed type lead accumulators of this invention were formed in the front face and the interior of a **** sheet of a glass fiber subject -- the distributed status -- uniform -- intervening -- the hole of a separator -- the role which forms structure into a complicated maze is borne

[0008] Moreover, inorganic fine particles need to have an electric insulation and sulfuric-acid-proof solubility, in order not to reduce the function as a separator. As a particle diameter of inorganic fine particles which satisfies these conditions, in order to make it placed between the interior of a sheet in the state of variance at a back process, it is more nearly required than the mean aperture of a **** sheet to use a parvus thing at least, and it is required to be 5 micrometers or less under a usual condition.

[0009] Moreover, although it is more desirable that it is complete within the limits of fixed width of face as for a particle diameter, substantially, the variation in the particle diameter in within the limits 5 micrometers or less does not affect especially many properties of the done separator, and also bears enough that in which the particle diameter differed [aforementioned] when it was within the limits at use.

[0010] Moreover, as inorganic fine particles with which it is satisfied of the above-mentioned conditions, sulfates, such as a calcium sulfate besides inorganic-acid ghosts, such as a silica, an alumina, and a titania, and a barium sulfate, can also be used.

[0011] in addition, the thing made to be uniformly placed between parts for the pore of a separator by the role of the inorganic fine particles of this invention in the state of variance -- the hole of a separator -- it is more advantageous for the specific gravity of the fine particles to use to use a parvus thing as much as possible from it being the purpose to bury a hole using the fine-particles grain which is to operate structure, and specified and prepared the particle diameter from the material cost side

[0012] Moreover, the role of the water-soluble mineral which combines with inorganic fine particles and is used is fixing inorganic fine particles on a glass fiber, and reducing the powder omission at the time of separator handling. Moreover, it has the role which raises dendrite-proof short nature as well as inorganic fine particles in water-soluble mineral.

[0013] In order to make inorganic fine particles and water-soluble mineral uniformly placed between parts for the pore formed in the front face and the interior of a **** sheet of a glass fiber subject in the state of variance, technique, such as carrying out impregnation processing of the liquid which sets a **** sheet at a back process after ****, distributed inorganic fine particles and water-soluble mineral, and was melted, is effective. Moreover, by the technique of processing fine particles at a back process, in order for fine particles not to bar a debt of fiber or not to bar the inorganic binder effect formed at the time of acid **** like the technique of mixing fine particles at the time of ****, there is an advantage from which the sheet of high intensity is obtained.

[0014] Moreover, when making inorganic fine particles and water-soluble mineral placed between **** sheets, if luminous efficacy is taken into consideration from a industrial field although the **** sheet of a glass fiber subject may be in the **** status even if it is in the wet paper web status, it is desirable [a sheet] to shift to a back process from a **** process with the wet paper web status in a series of facility equipment with which the **** process and the back process were connected.

[0015] Moreover, as for the abundance of the inorganic fine particles in a separator, it is desirable that it is five to 50 capacity [of the pure volume of the separator which is the sum of the volume of a glass fiber and inorganic fine particles] %. the hole formed in a separator under by 5 capacity % -- since maze structure with sufficient structure to attain the purpose is not acquired, it is not desirable In 50 capacity % **, since the voids of a separator falls, electric resistance is raised and the high-rate-discharge property of a cell is reduced, it is not desirable.

[0016] Moreover, as water-soluble mineral, the sulfates added in the electrolytic solution as a short inhibitor from the former are suitable from the field of fixation of fine particles, and the enhancement effect of short-proof nature.

[0017] Moreover, as for the coating weight of water-soluble mineral, it is desirable to consider as 0.5 - 10% of the weight of a domain to the separator weight in an inorganic fine-particles lump. Since less than 0.5 % of the weight of the fixed effect to the glass fiber of inorganic fine particles is insufficient, at it, it is not desirable. Since there is a risk of a separator becoming hard too much in ** 10% of the weight, and producing a crack at the time of a U character bending, it is not desirable.

[0018]

[Example] Hereafter, this invention is explained in detail based on an example.

(Example 1) Using 90 % of the weight of the glass fibers of 0.7 micrometers of the diameters of mean fiber, and 10 % of the weight of the **** adhesion fiber made from polyester, wet **** of the glass fiber sheet with a thickness of 0.5mm was carried out, and it was produced. Next, inorganic fine-particles SiO₂ concentration impregnated this glass fiber sheet 0.9% of the weight in the processing liquid which sodium-sulfate concentration adjusted so that it might become 0.2 % of the weight, after adjusting a water content so that processing liquid may serve as adhesion of the amount of 5 times of a glass fiber sheet weight, it dried using the 150-degree C compartment dryer, and the separator was obtained.

[0019] (Example 2) The separator was obtained like the aforementioned example 1 except having made inorganic fine-particles SiO₂ concentration of the aforementioned processing liquid, and having made sodium-sulfate concentration into 0.2 % of the weight 3.5% of the weight.

[0020] (Example 3) The separator was obtained like the aforementioned example 1 except having made inorganic fine-particles SiO₂ concentration of the aforementioned processing liquid, and having made sodium-sulfate concentration into 0.6 % of the weight 11% of the weight.

[0021] (Example 4) The separator was obtained like the aforementioned example 1 except having made inorganic fine-particles SiO₂ concentration of the aforementioned processing liquid, and having made sodium-sulfate concentration into 3 % of the weight 11% of the weight.

[0022] (Example 1 of a comparison) Using the glass fiber of 0.7 micrometers of the diameters of mean fiber, wet **** of the glass fiber sheet with a thickness of 0.5mm was carried out, and the separator was obtained.

(Example 2 of a comparison)

[0023] In the example 1, the separator was obtained like the aforementioned example 1 except having made inorganic fine-particles SiO₂ concentration of the aforementioned processing liquid, and having made sodium-sulfate concentration into 0 % of the weight 10% of the weight.

[0024] (Example 3 of a comparison) After carrying out the mixed variance of the glass fiber of 0.7 micrometers of the diameters of mean fiber, and the SiO₂ fine particles underwater, the adsorbent was added, adsorption operation of fine particles was performed, and the separator which consists of a **** sheet with a thickness of 0.5mm was obtained.

[0025] (Example 4 of a comparison) Using 100 % of the weight of the glass fibers of 0.7 micrometers of the diameters of mean fiber, wet **** of the glass fiber sheet with a thickness of 0.5mm was carried out, and it was produced. Next, it impregnated in the processing liquid which adjusted this glass fiber sheet so that sodium-sulfate concentration might become 2%, and after adjusting a water content so that processing liquid may serve as adhesion of the amount of 5 times of

a glass fiber sheet weight, it dried using the 150-degree C compartment dryer, and the separator was obtained.

[0026] Next, in order to check the effect of the separator for sealed type lead accumulators of this invention, it examined by producing the cell of cell capacity 60Ah at intervals of [of 0.4mm] seven negative plates, six anode plates, and the plate using the above-mentioned separator. The test result is shown in Table 1.

[0027] In addition, about the test method, it was performed as follows.

It measured by the [maximum aperture] bubble-point method.

It measured using [mean aperture] liquid porosimeter equipment.

[Electric resistance] JIS It measured by the technique based on C2313.

[Cycle-life] JIS It measured based on heavy-loading life test specified to D5301.

[Rate electric discharge property of for 10 minutes] The electric discharge persistence time (part) until a discharge final voltage becomes 7.8V on condition that 25 degrees C and discharge current 180A was found.

[0028]

[Table 1]

No	項目	単位	実施例1	実施例2	実施例3	実施例4	比較例1	比較例2	比較例3	比較例4
1	デンドライト防止法	—	粉体+硫酸塩系着				なし	粉体着	粉体着	(硫酸塩)
2	ガラス繊維シート	wt%	95.5	85	65	65	—	65	—	100
3	0.7 μ mガラス繊維	wt%	—	—	—	—	100	—	80	—
4	SiO ₂ 粉体	wt%	4.5	15	35	35	0	35	20	—
5	硫酸ナトリウム	外wt%	1	1	2	10	0	0	0	10
6	SiO ₂ 粉体の体積	vol%	5.2%	17.1%	38.7%	38.7%	—	38.7%	24.1%	—
7	厚さ	mm	0.51	0.51	0.50	0.50	0.51	0.50	0.50	0.50
8	坪量	g/m ²	85	96	125	141	82	141	84	90
9	見掛け密度	g/cm ³	0.167	0.188	0.250	0.282	0.161	0.282	0.168	0.180
10	最大孔径	μ m	15.4	15.7	15.2	15.2	15.3	15.2	15.3	15
11	平均孔径	μ m	4.1	3.9	4.0	4.0	4.2	4.0	4.1	4.2
12	電気抵抗	$\Omega \cdot 100\text{cm}^2/\text{枚}$	0.00020	0.00025	0.00035	0.00040	0.00020	0.00050	0.00022	0.00035
13	引張強度	MPa	0.7	0.7	0.7	0.7	0.5	0.7	0.2	0.6
14	折り曲げ割れ	—	無し	無し	無し	無し	無し	無し	無し	有り
15	粉体発塵・粉体ち	—	無し	無し	無し	無し	無し	多い	若干有り	—
16	サイクル寿命	サイクル	340	368	470	580	300	580	305	組立不可
17	10分間率放電	min	10.2	9.8	9.3	9.0	10.2	9.0	10	—

比較例1は化成中に短絡発生するものがあった。

[0029] In the separator of the example to which ** arrival of inorganic fine particles and the sulfate was carried out in order to give dendrite-proof short nature with a thin shape so that clearly from Table 1, compared with the separator of the example of a comparison, there is no powder omission at the time of handling, and workability, such as U character bending, was not spoiled, either, but what ** had also exceeded the cycle life, without also affecting cell properties, such as electric resistance and a rate electric discharge property of for 10 minutes. In addition, since the separator fractured in the separator of the example 4 of a comparison at the time of a U character bending, a cell property cannot be evaluated.

[0030]

[Effect of the invention] The separator for sealed type lead accumulators of this invention has the following effects.

(1) Since the separator for sealed type lead accumulators of this invention is made from a back process after **** in the sheet of a detailed glass fiber subject by carrying out impregnation processing of the inorganic fine particles at dispersed liquid, it can make inorganic fine particles uniformly placed between parts for the pore of the front face of a **** sheet, and the interior. for this reason, the hole of a separator -- the distance (namely, time) taken to be able to form structure into a complicated maze, to be able to prevent that PbSO₄ crystal penetrates the interior of a separator linearly, and for a dendrite to penetrate a separator, and to connect between two-poles plates -- it can work -- coming -- a dendrite -- a short incidence rate can be reduced and the life extension of a cell can be planned

(2) Like [in the case of twisting the sheet of a detailed glass fiber subject by the conventional mixing method from being made by processing inorganic fine particles at a back process after ****], since the separator for sealed type lead accumulators of this invention does not check a debt of the fiber of a fiberglass-mat sheet, it cannot reduce a separator intensity and can maintain good cell assembly nature.

(3) By using these inorganic fine particles with the water-soluble mineral which acts also as a short inhibitor, since inorganic fine particles are fixable in a separator, there is no powder omission at the time of separator handling, and enhancement in a work environment can be aimed at. Moreover, there is an advantage which does not spoil U character bendability even if it makes a lot of sulfates **** to a fiberglass-mat separator as compared with the case where adhesion processing of the sulfate is carried out independently, in order that inorganic fine particles may work as a support of water-soluble mineral in this case.

(4) Since it excels in a thin shape at dendrite-proof short nature, there is no powder omission, the sealed type lead accumulator separator of high intensity is obtained and high-capacity-izing of a sealed type lead accumulator and much more enhancement in a high-rate-discharge property can be realized in this way by making both inorganic fine particles and water-soluble mineral intervene and hold on a fiberglass-mat sheet, a industrial value is large.

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CLAIMS

[Claim]

[Claim 1] It is the separator for sealed type lead accumulators characterized by being the separator for sealed type lead accumulators which made inorganic fine particles placed between the sheets of the detailed glass fiber subject which carried out wet **** and was obtained in the state of variance, and these inorganic fine particles being fixed by water-soluble mineral in the void of this sheet.

[Claim 2] The aforementioned water-soluble mineral is the separator for sealed type lead accumulators of the claim 1 publication characterized by existing after the aforementioned inorganic fine-particles front face has mainly ****ed.

[Claim 3] The claim 1 characterized by the amount of the aforementioned inorganic fine particles being five to 50 capacity [of the pure volume of a separator] %, or the separator for sealed type lead accumulators given in two.

[Claim 4] The claim 1 to which the aforementioned inorganic fine particles are electric insulations, and are characterized by being the inorganic fine particles of sulfuric-acid-proof solubility, or the separator for sealed type lead accumulators given in either of 3.

[Claim 5] The separator for sealed type lead accumulators of claim 4 publication with which the aforementioned inorganic fine particles are characterized by being a silica, an alumina, or a titania.

[Claim 6] The claim 1 characterized by the particle diameter of the aforementioned inorganic fine particles being 5 micrometers or less, or the separator for sealed type lead accumulators given in either of 5.

[Claim 7] The claim 1 characterized by the aforementioned water-soluble mineral being the sulfate which acts as a short inhibitor, or the separator for sealed type lead accumulators given in either of 6.

[Claim 8] The claim 1 to which the aforementioned water-soluble mineral is characterized by containing 0.5 to 10% of the weight to the separator weight in an inorganic fine-particles lump, or the separator for sealed type lead accumulators given in either of 7.

[Claim 9] The claim 1 characterized by being what obtained by carrying out impregnation processing of the fiberglass-mat sheet which considered as the main material, carried out wet **** of the detailed glass fiber, and obtained it, and drying it in the liquid which distributed and prepared inorganic fine particles and water-soluble mineral, or the separator for sealed type lead accumulators given in either of 8.

[Claim 10] The separator for sealed type lead accumulators of the claim 9 publication characterized by carrying out impregnation processing of the aforementioned fiberglass-mat sheet at the liquid which distributed inorganic fine particles and water-soluble mineral, and was prepared so that it may become 1 - 9 % of the weight in the concentration of inorganic fine particles about the concentration of 1 - 15 % of the weight, and water-soluble mineral.

[Translation done.]